Direct nanocomposite of crystalline TiO_2 particles and mesoporous silica as a molecular selective and highly active photocatalyst

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Well-crystallised TiO_2 particles (P-25, 20–30 nm in diameter) were directly incorporated into surfactant-templated mesoporous silica particles (pore diameter: 2.7 nm), and the composite material with a high TiO_2 content (60 wt%) showed molecular selective and enhanced photocatalysis for decomposition of 4-nonylphenol.

Since the discovery of mesoporous silicates such as MCM-41[1] and FSM-16,[2] their well-controlled nanostructures have been a subject of great interest because of potential applications as host structures, adsorbents, and catalysts for reactions involving large molecules.[3–7] To develop new catalytic functions for mesoporous silicates, many studies have been carried out on the loading of active species such as transition metal oxides[8–15] and organic/organometallic active sites[3,5,6,16,17] on the nanostructured silicates. Since Ti species are active for hydrocarbon oxidation and TiO_2 is well known as a versatile photocatalyst,[18–22] many researchers have attempted to combine titanium oxide with mesoporous silicas by various methods such as simple impregnation, the sol-gel method and surface grafting.[10–15] However, it does not seem to be easy to produce materials of this type that exceed the photocatalytic performance of well-crystallized pure TiO_2 particles such as commercially available "P-25". This is due to low crystallinity of the TiO_2 particles on the mesoporous supports and a limitation in the TiO_2 loading level (*ca.* 10 wt%).

Here we report a novel type of composite material consisting of TiO_2 particles and organo-templated mesoporous silica: highly active TiO_2 crystalline particles (P-25) are directly incorporated into mesoporous silica particles. This material shows molecular selective photocatalysis for decomposition of organic molecules such as 4-nonylphenol, an endocrine disrupter present in water. The TiO_2 content was able to reach more than 60 wt%, and the synthetic procedures were very simple. The composite catalyst showed a higher activity for the decomposition of 4-nonylphenol than a mechanical mixture of TiO_2 and mesoporous silica.

Mesoporous silica (MPS) and the composite catalysts (TiO2MPS-X, X = 30 or 60, where X is the TiO_2 content (wt%) in the composite catalyst) were prepared by the following procedure: 4.4 g of hexadecyltrimethylammonium bromide was combined with *ca.* 230 g of hot water, 17 g of 35% ammonia solution and a weighted amount (2.1 or 7.3 g) of TiO_2 (Degussa P-25). The TiO_2 was ultrasonically dispersed in the solution. After adjusting the pH to 11.8 by adding ammonia solution, 17 g of tetraethoxysilane (TEOS) was quickly added to the mixture, under vigorous stirring. After aging for 1 h, the precipitate was filtered, washed with water, and dried at 353 K for one day. The materials were calcined at 813 K for 6 h to obtain the mesoporous composite materials. MPS was prepared by the same procedure, but no TiO_2 was added. Nitrogen adsorption isotherms were measured at 77 K. TEM images were taken with a JEM-2010 transmission electron microscope (JEOL). Photocatalytic tests were carried out as follows: typically, 30 mg of the composite photocatalyst was added to 300 g of a mixed aqueous solution of 4-nonylphenol, 4-*n*-heptylphenol, 4-*n*-propylphenol, and phenol (their initial concentrations were $1.4-1.6 \times 10^{-5}$ mol dm^{-3}). After adsorption of the phenols onto the catalysts had reached equilibrium, the mixture was irradiated with a 300 W Xe lamp, under stirring. The solution was analyzed using an HPLC instrument equipped with a UV detector (Shimadzu LC-10). For comparison, a mechanical mixture of MPS and TiO_2 (P-25) was also used as a photocatalyst.

Nitrogen adsorption isotherms (left panel) and X-ray diffraction patterns (right panel) of TiO2MPS-30, TiO2MPS-60, and MPS are shown in Fig. 1. As shown in the left panel of Fig. 1, the composite catalysts had nitrogen adsorption isotherms with sharp steps, demonstrating that they have uniform mesopores. The mesopore volumes were determined from the adsorption isotherms to be 0.54 and 0.31 cm^3 g^{-1} for TiO2MPS-30 and TiO2MPS-60, respectively. These values correspond to 80 and 45% of the pore volume of MPS. Considering the silica contents in these samples (70 and 40 wt%), this strongly indicates that the mesoporosity per silica weight was similar or slightly larger in the two samples compared to MPS. In other words, the addition of TiO_2 particles to MPS did not reduce the porosity of the silica moiety. BJH analysis of these three isotherms gave pore diameters of around 2.7 nm. As shown in the right panel of Fig. 1, TiO2MPS-30 and TiO2MPS-60 had weaker X-ray diffraction peaks than MPS (note

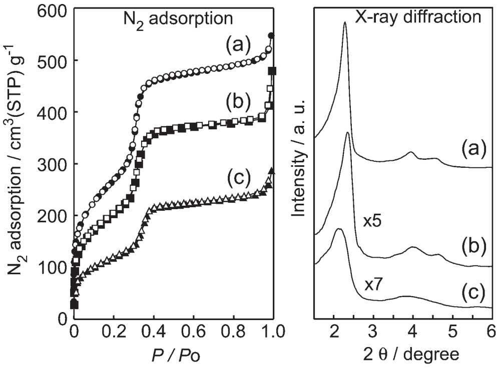

Fig. 1 Nitrogen adsorption isotherms (left panel) and X-ray diffraction patterns (right panel) of mesoporous silica and the composite materials: MPS (a), TiO2MPS-30 (b), and TiO2MPS-60 (c).

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the magnification indicated in the figure). This indicates that these composite catalysts have less hexagonally-ordered mesopores than MPS. Therefore the results shown in Fig. 1 show that the addition of TiO_2 particles to MPS did not interfere with the formation of mesoporous silica, but it did disturb the hexagonal ordering of the pores to some extent.

In order to obtain more information on the structure of the sample, TEM observation of TiO2MPS-60 was carried out. Most TiO_2 particles were incorporated into the silica porous moiety. As shown in Fig. 2a, it was clearly observed that crystalline TiO_2 particles were surrounded by mesoporous silica. TEM observation revealed that the TiO_2 particles were incorporated into the porous silica as illustrated schematically in Fig. 2b.

Fig. 3 shows the photocatalytic activity of TiO2MPS-60 for the decomposition of a mixed aqueous solution of several alkylphenols. For comparison, the activity of a mechanical mixture of MPS and TiO_2 with the same stoichiometric composition as that of TiO2MPS-60, was also measured. As shown in Fig. 3b, the mechanical mixture showed almost the same decomposition rate for all the kinds of phenols contained in the solution: the initial rates were 1.6, 1.8, 1.5, and 1.6 $\times$ 10^{-7} mol min^{-1} for 4-nonylphenol, 4-*n*-heptylphenol, 4-*n*-propylphenol, and phenol, respectively. In other words, the photocatalytic decomposition is non-selective. On the other hand, TiO2MPS-60 exhibited higher decomposition rates for 4-nonylphenol and 4-*n*-heptylphenol than for the other phenols (Fig. 3a). The initial decomposition rates in Fig. 3a were 2.2, 2.3, 1.3, and 0.66 $\times$ 10^{-7} mol min^{-1} for 4-nonylphenol, 4-*n*-heptylphenol, 4-*n*-propylphenol, and phenol, respectively. Of the alkylphenols tested here, molecules having a larger alkyl group were decomposed at a higher rate. These results demonstrated that TiO2MPS-60 showed molecular selective photocatalysis. Moreover, the difference between TiO2MPS-60 and the mechanical mixture strongly suggests that the molecular selectivity is attributable to the structure of TiO2MPS-60, in which the TiO_2 particles are incorporated into the porous silica (Fig. 2).

It should be noted that the decomposition rates of 4-nonylphenol and 4-*n*-heptylphenol shown in Fig. 3a are faster than those shown in Fig. 3b: the composite catalyst showed higher activity than the mixture. In other words, incorporation of TiO_2 into the mesoporous silica enhanced the photocatalytic activity for the decomposition of these molecules. On the other hand, the decomposition rates of phenol and 4-*n*-propylphenol were reduced by the incorporation. This acceleration and deceleration could be explained by the adsorption affinity toward the mesoporous silica. 4-Nonylphenol and 4-*n*-heptylphenol are large, hydrophobic molecules, and are preferentially concentrated into the mesoporous silica. Thus, their decomposition was accelerated. This idea is consistent with the adsorption behaviours that were observed before the photoirradiation in Fig. 3. The catalyst reported here is completely inorganic, and therefore free of the durability problem associated with an organo-grafted molecular selective photocatalyst.[23,24] Most recently, SBA-15 thin films containing TiO_2 particles (less than 30 wt%) were reported and they showed lower activity than pristine TiO_2 particles,[25] indicating that the performance of the nanocomposite in the present work is remarkable.

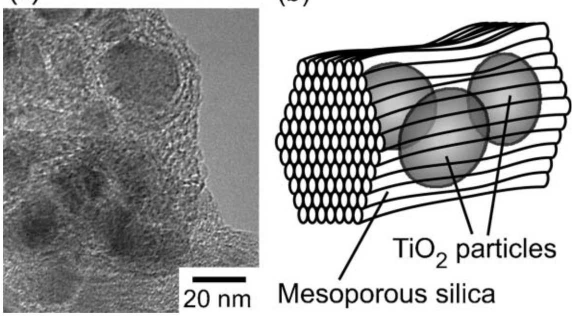

Fig. 2 TEM image of TiO2MPS-60 (a), and schematic illustration of the composite materials (b).

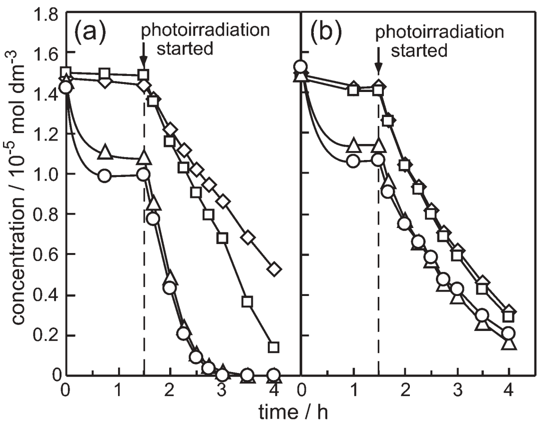

Fig. 3 Photocatalytic decomposition of alkylphenols by 30 mg TiO2MPS-60 (a), and by a mechanical mixture of TiO_2 (18 mg) and MPS (12 mg) (b). Circles, 4-nonylphenol; triangles, 4-*n*-heptylphenol; squares, 4-*n*-propylphenol; diamonds, phenol.

In conclusion, TiO_2 particles were directly incorporated into mesoporous silica particles, and this novel composite material showed molecular selective photocatalysis toward the decomposition of alkylphenols. These results highlight that the direct incorporation of catalytically active nanoparticles into mesoporous materials is a promising strategy for designing new catalysts. Tuning of the molecular selectivity of the catalyst by controlling the pore diameter is an interesting subject now under investigation.

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